

This is a repository copy of *Filling a niche in "ligand space" with bulky, electron-poor phosphorus (III) alkoxides*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/138201/>

Version: Accepted Version

---

**Article:**

Slattery, John Martin orcid.org/0000-0001-6491-8302, Hussein, Sharifa, Priester, Denis et al. (6 more authors) (2018) Filling a niche in "ligand space" with bulky, electron-poor phosphorus (III) alkoxides. Chemistry : A European Journal. ISSN 1521-3765

<https://doi.org/10.1002/chem.201804805>

---

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

# Filling a niche in “ligand space” with bulky, electron-poor phosphorus (III) alkoxides

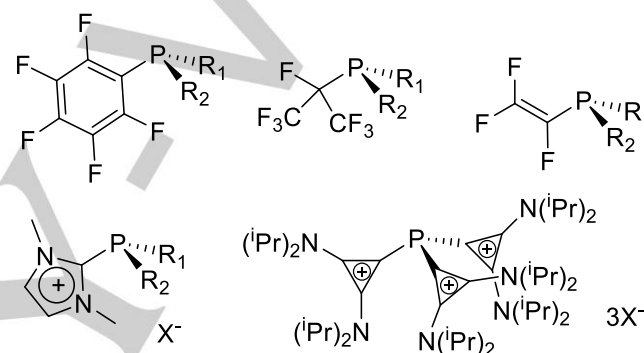
Sharifa Hussein,<sup>[a]</sup> Denis Priester,<sup>[a]</sup> Paul Beet,<sup>[a]</sup> Jonathon Cottom,<sup>[a]</sup> Sam J. Hart,<sup>[a]</sup> Tim James,<sup>[a]</sup> Robert J. Thatcher,<sup>[a]</sup> Adrian C. Whitwood<sup>[a]</sup> and John M. Slattery,<sup>\*,[a]</sup>

**Abstract:** The chemistry of phosphorus(III) ligands, which are of key importance in coordination chemistry, organometallic chemistry and catalysis, is dominated by relatively electron-rich species. Many of the electron-poor P(III) ligands that are readily available have relatively small steric profiles. As such, there is a significant gap in “ligand space” where more sterically bulky, electron-poor P(III) ligands are needed. This contribution discusses the coordination chemistry, steric and electronic properties of P(III) ligands bearing highly fluorinated alkoxide groups of the general form  $\text{PR}_n(\text{OR}^F)_{3-n}$ , where  $\text{R} = \text{Ph}$ ,  $\text{R}^F = \text{C}(\text{H})(\text{CF}_3)_2$  and  $\text{C}(\text{CF}_3)_3$ ;  $n = 1-3$ . These ligands are simple to synthesize and a range of experimental and theoretical methods suggest that their steric and electronic properties can be “tuned” by modification of their substituents, making them excellent candidates for large, electron-poor ligands.

## Introduction

Phosphorus(III)-centered Lewis bases are amongst the most commonly encountered ligands in organometallic chemistry and catalysis. The ability to “tune” the steric and electronic properties of these ligands by modification of the ligand substituents allows the properties of a metal complex to be tailored to suit a particular application. According to the Orpen-Connelly model,<sup>[1]</sup> P(III) ligands are  $\sigma$ -donors through their lone pairs and  $\pi$ -acceptors through their P-R  $\sigma^*$ -orbitals. The degree of  $\sigma$ -donor/ $\pi$ -acceptor character for a particular ligand can be influenced by the substituents at phosphorus e.g. through inductive effects or by changing the relative energies of the frontier orbitals. Similarly, the size of the substituents has a profound influence on the steric properties of these ligands. In order to facilitate the application of P(III) ligands a number of parameters may be used to describe these steric and electronic properties. Ligand “cone angles”,  $\text{S}_4'$  and  $\text{He}_8$  parameters, amongst others, are frequently used to describe steric properties.<sup>[2]</sup> The CO stretching vibrations of metal-carbonyl complexes e.g.  $[\text{Ni}(\text{L})(\text{CO})_3]$ ,  $[\text{W}(\text{L})(\text{CO})_5]$ ,  $[\text{Rh}(\text{L})(\text{CO})_2\text{Cl}]$  and  $[\text{CpIr}(\text{L})(\text{CO})]$ , where L = the ligand of interest, or other spectroscopic features such as metal-phosphorus coupling constants are commonly used as indicators of electronic

properties.<sup>[2f, 2i, 3]</sup> When combined, these data can provide a stereo-electronic map of phosphine “ligand space” that can be used to link structure to function and aid in the design of ligands and complexes for particular applications. Such design principles are exemplified in concepts such as Ligand Knowledge Bases (LKBs).<sup>[2h, 2i, 4]</sup>



**Figure 1.** Selected examples of electron-poor P(III) ligand systems that have been explored.  $\text{R}_1$  and  $\text{R}_2$  are a range of alkyl, aryl or heteroatom-based functional groups and  $\text{X}^-$  is a suitable anion.

It has been noted, when considering a map of ligand space, derived from computed steric and electronic parameters, that a large proportion of available P(III) ligands are species that are relatively electron rich.<sup>[2f]</sup> The electron-poor P(III) ligands available are often relatively small, e.g.  $\text{P}(\text{CF}_3)_3$  (cone angle =  $137^\circ$ ). Therefore, there exists a significant gap in ligand space corresponding to electron-poor, sterically bulky P(III) ligands. These species are expected to be relatively poor  $\sigma$ -donors and stronger  $\pi$ -acceptors than typical phosphines such as  $\text{PPh}_3$ . Thus, their ability to bind to, and stabilize, metals in low oxidation states or to generate highly electrophilic metal centers is enhanced. Likewise, their steric bulk may promote the dissociation of other ligands (e.g. in catalysis) or stabilize low-coordinate metal centers.

Several groups have attempted to fill this gap in ligand space, e.g. with ligands such as those in Figure 1. One approach has been to prepare P(III) ligands bearing perfluorinated *tert*-butyl, *iso*-propyl and *cyclo*-hexyl substituents.<sup>[2f, 5]</sup> However, studies involving these ligands are still relatively rare and their syntheses are often not trivial. Brisdon *et al.* and others have worked extensively on perfluorovinyl-containing phosphines ( $\text{PR}_{3-n}(\text{vinyl}^F)_n$  {where  $\text{R} = \text{Ph}$ ,  $\text{NMe}_2$ ,  $\text{NEt}_2$ ,  $\text{EtO}$ ,  $^i\text{Pr}$ ,  $\text{Cy}$ ,  $\text{BuO}$ ;  $n = 1, 2$ ;  $\text{vinyl}^F = \text{CF}=\text{CF}_2$ ,  $\text{CCl}=\text{CF}_2$ ,  $\text{CF}=\text{CFH}$ ,  $\text{CCCF}_3$ } and the P-stereogenic phosphine  $^n\text{BuPhP}(\text{CF}=\text{CF}_2)$ .<sup>[5d, 6]</sup> These perfluorovinyl groups were found

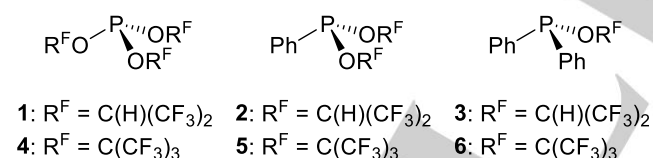
[a] Dr S. Hussein, Mr D. Priester, Dr J. Cottom, Mr S. J. Hart, Mr T. James, Dr R. J. Thatcher, Dr A. C. Whitwood and Dr. J. M. Slattery. Department of Chemistry, University of York, Heslington, York YO10 5DD (UK). Fax: (+44) 01904 322516. E-mail: [john.slattery@york.ac.uk](mailto:john.slattery@york.ac.uk)

Supporting information for this article is given via a link at the end of the document.

to be quite electron withdrawing, similar electronically to alkoxy groups. However, the origin of their similar electronic properties is different: perfluorovinyl groups have an inductive effect that withdraws electron density from the P lone pair (leading to weaker  $\sigma$ -donation), while alkoxy groups reduce the energy of the  $\sigma^*$ -orbital (leading to better  $\pi$ -acceptor character). Sterically, perfluorovinyl groups are smaller than a perfluorinated phenyl group.

An alternative approach to the use of fluorinated, electron-withdrawing groups in the preparation of electron-poor phosphines has been to include cationic groups at phosphorus. The area of  $\alpha$ -cationic phosphines has seen tremendous growth in recent years and has uncovered some exciting ligands whose strongly electron-withdrawing properties have unlocked novel catalytic processes.<sup>[7]</sup> While these are undoubtedly exciting ligands, they also have some disadvantages, which mean they will not be appropriate for all situations. These include changes in solubility compared to neutral species, weaker M-L bonding and the potential for unwanted reactions at the cationic component. In addition, the more highly charged ligands, which are the most electron poor, have so far displayed only limited coordination chemistry. As such, there is still significant scope for the development bulky P(III) ligands that are electron poor and simple to synthesize to complement existing species and help to fill the gap in ligand space.

This paper discusses the coordination chemistry, steric and electronic properties of a series of phosphite, phosphonite and phosphinite ligands with the general formula  $\text{PR}_{3-n}(\text{OR}^F)_n$  ( $\text{R} = \text{Ph}$ ,  $\text{R}^F = \text{C}(\text{CF}_3)_3$ ,  $\text{C}(\text{H})(\text{CF}_3)_2$ ;  $n = 1-3$ ) (Figure 2) using a combination of experimental and theoretical approaches. These species are simple to synthesize and the fluorinated alkoxy groups impart both steric bulk, and significant  $\pi$ -acceptor character to the ligands. The steric and electronic properties of these species can be tuned by varying R and  $\text{R}^F$ .



**Figure 2.** Phosphorus ligands investigated in this work.

The chemistry of fluorinated phosphorus alkoxides has a long history and compounds **1**, **2**, **3** and **4** have previously been described.<sup>[8]</sup> However, their ligand chemistry and catalytic applications are not well developed. To the best of our knowledge **5** and **6** have not previously been reported. Of all the ligands that are known, the catalytic applications of  $\text{P}\{\text{OCH}(\text{CF}_3)_2\}_3$  **1** have been investigated in the most detail. In early work, van Leeuwen investigated the use of **1** as a ligand in the Ni-catalysed cyclodimerisation of isoprene.<sup>[9]</sup> However, the observed yields were quite low. The same group later found that **1**, along with other sterically bulky, electron-poor ligands, formed highly active hydroformylation catalysts with Rh.<sup>[10]</sup> Ligand **1** has also been used successfully in catalytic systems for [4+2]

cycloaddition reactions, for example those involving substrates that are electronically not well differentiated.<sup>[11]</sup> Recent work has shown that **1** can play an important role in the development of active catalysts for C-H functionalization reactions, primarily with Rh-based systems, but also with Pd.<sup>[11f, 11g, 12]</sup> As part of this work, Yanagisawa *et al.* demonstrated that the use of very bulky, electron-poor ligands appears to be essential for successful catalysis when  $[\text{RhCl}(\text{CO})\text{L}_2]$ , where  $\text{L} = \mathbf{1}$ , **2** and **3**, complexes are used as catalysts for the direct C-H coupling of heteroarenes with haloarenes.<sup>[12a]</sup> When  $\text{L} = \mathbf{1}$ , 94 % conversions can be achieved, but when the number of fluorinated alkoxy groups at P are reduced (i.e. when  $\text{L} = \mathbf{2}$ ) conversions drop to 31 % and no conversion is seen for  $\text{PPh}_3$  for the same substrates. It has also been possible to utilize **1** for the Ir-catalysed hydrosilylation of amides.<sup>[13]</sup>

## Results and Discussion

Synthetic routes to compounds **1-3** have previously been reported by reaction of  $\text{PPh}_{3-n}\text{Cl}_n$  ( $n = 1-3$ ) with either  $\text{LiOC}(\text{H})(\text{CF}_3)_2$  or  $\text{HOC}(\text{H})(\text{CF}_3)_2$  and  $\text{NEt}_3$ . However, in our hands, reaction of the relevant P-chlorophosphine with  $\text{NaOC}(\text{H})(\text{CF}_3)_2$  in dry, degassed  $\text{CH}_2\text{Cl}_2$  under ultrasonic activation has proved the most convenient approach. Compound **4** has previously only been synthesized by reaction of  $\text{PCl}_3$  with  $\text{ClOC}(\text{CF}_3)_3$ .<sup>[14]</sup> The preparation of this hypochlorite, from  $\text{ClF}$  and  $\text{HOC}(\text{CF}_3)_3$  with the elimination of  $\text{HF}$ , makes this route less accessible for standard synthetic labs and it was pleasing to find that reaction of 3 equivalents of  $\text{NaOC}(\text{CF}_3)_3$  with  $\text{PCl}_3$  also gives **2**. Compounds **5** and **6** have, to the best of our knowledge, not been reported previously and can be synthesized in a similar manner. Although all compounds reported here can be purified by distillation (sublimation in the case of **4**) it is often possible to use the ligands as prepared in  $\text{CH}_2\text{Cl}_2$  solution, after filtration to remove  $\text{NaCl}$ , without further purification. The  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectroscopic data for each compound can be found in Table 1.

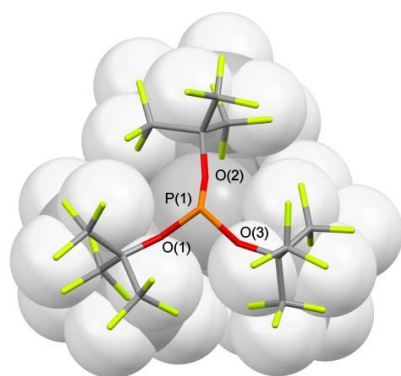
**Table 1.** Spectroscopic data and isolated yields for ligands **1-6**.

Ligand	Isolated Yield (%)	$\delta$ $^{31}\text{P}\{^1\text{H}\}$ (ppm)	$\delta$ $^{19}\text{F}$ (ppm)	$\delta$ $^1\text{H}$ (ppm) <sup>[a]</sup>
1	39 <sup>[b]</sup>	140	-74.7	4.80
2	61	190	-74.3 and -74.1 <sup>[c]</sup>	4.64
3	70	143	-73.8	4.71
4	53	149	-72.3	NA
5	69	190	-71.4	NA
6	69	132	-71.7	NA

[a] Selected  $^1\text{H}$  NMR chemical shifts, for  $\text{OC}(\text{H})(\text{CF}_3)_2$  groups only, are reported. [b] Although  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectroscopy suggests that the formation of **1** is quantitative, the volatility of **1** means that loss of some product under vacuum is difficult to avoid during isolation. [c] Two

environments are observed for each C(H)(CF<sub>3</sub>)<sub>2</sub> group in the <sup>19</sup>F NMR of **2**, due to atropisomerism because of hindered rotation around either the P-O or O-C bond.

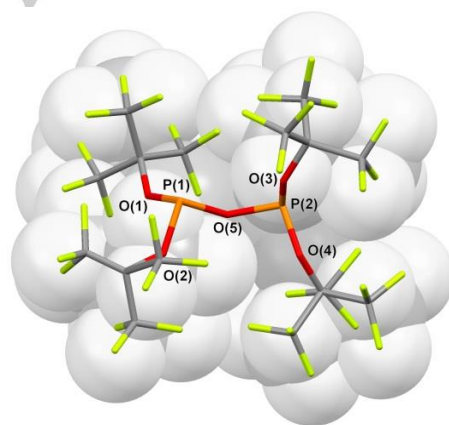
While **1**, **2**, **3**, **5** and **6** are liquids under standard conditions, **4** is a solid that crystallizes readily from CH<sub>2</sub>Cl<sub>2</sub> solution. Although significant disorder (even at low temperature) appears to be present in all crystals of **4** grown under a variety of conditions, it was possible to obtain a single-crystal X-ray structure of this compound of suitable quality to establish structural connectivity (Figure 3). While a full discussion of the structural parameters of **4** is not appropriate given the quality of the model, the geometry around phosphorus appears to be similar to related aryl phosphites (e.g. P(OPh)<sub>3</sub>, av. P-O 1.604 Å)<sup>[15]</sup> A space-fill representation of the structure of **4** (superimposed on Figure 3) suggests that **4** is a very sterically bulky ligand. In addition, the perfluoro-*t*-butoxide substituents appear to have little room for conformational flexibility, which suggests that this phosphite should have a relatively rigid steric profile compared to many phosphites..



**Figure 3.** Single-crystal X-ray structure of P{OC(CF<sub>3</sub>)<sub>3</sub>}<sub>3</sub> (**4**). Monoclinic, C2/c, 110 K, R<sub>1</sub> = 0.1565, wR<sub>2</sub> = 0.4462. Whole-molecule disorder (modelled over two positions) in addition to CF<sub>3</sub> rotational disorder, is present in the structure. Only one position is shown (and bond lengths and angles given for this) for clarity. Selected bond lengths (Å) and angles (°): P(1)-O(1) 1.609(11), P(1)-O(2) 1.615(11), P(1)-O(3) 1.610(12), O(1)-P(1)-O(2) 92.8(6), O(1)-P(1)-O(3) 93.0(6), O(2)-P(1)-O(3) 94.1(6).

The free ligands **1-6** are susceptible to hydrolysis, but unlike many electron-rich P(III) ligands do not appear susceptible to oxidation in air. In the case of **4**, it was possible to identify a product of partial hydrolysis, the pyrophosphite (R<sup>F</sup>O)<sub>2</sub>P-μO-P(OR<sup>F</sup>)<sub>2</sub> {R<sup>F</sup> = C(CF<sub>3</sub>)<sub>3</sub>} (**7**) in NMR spectroscopic (<sup>31</sup>P{<sup>1</sup>H} NMR δ = 135 ppm; <sup>19</sup>F NMR δ = -71.4 ppm) studies and crystals of this species were fortuitously obtained from a reaction involving **4** where small amounts of water were inadvertently introduced. This species gives some insight into the mechanism of hydrolysis, but also suggests the possibility that bidentate analogues of **4** may be accessible via a suitable synthetic route. **7** has a characteristic multiplet at 135 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and crystals suitable for X-ray structural analysis were grown from CH<sub>2</sub>Cl<sub>2</sub> solution (Figure 4).

As with the single-crystal X-ray structure of **4**, all crystals of **7** are heavily disordered, even at 110 K. In the case of **7**, this was modelled with the entire phosphorus-oxygen core being disordered over two positions (each with 50 % occupancy). As the model is still relatively poor, an extensive structural description is not appropriate. However, the data serve to confirm structural connectivity and suggest that the phosphorus centers exhibit distorted pyramidal geometries (with smaller O-P-O angles than in an ideal tetrahedral geometry). In addition, the phosphorus lone pairs point in opposite directions to each other, presumably as a consequence of the steric bulk of the two large -OC(CF<sub>3</sub>)<sub>3</sub> groups at each phosphorus center. Structurally characterized examples of free, uncoordinated pyrophosphites are very rare. To the best of our knowledge only one previous example is present in the Cambridge Structural Database, the sterically congested pyrophosphite 6-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)oxy]-2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[d,f][1,3,2]-dioxaphosphepin (CSD identifier MKSUU) reported by DeBellis *et al.*<sup>[16]</sup> This displays a similar phosphorus-oxygen core conformation to that shown by **7**, with P-lone pairs pointing away from each other. Although any comparison of structural parameters is tentative, given the quality of the data for **7**, it appears that the P-O distances and O-P-O angles in **7** are comparable to those reported by DeBellis (although any subtle effects due to the inclusion of fluorinated alkoxides would not be identifiable in these data).



**Figure 4.** Single-crystal X-ray structure of (R<sup>F</sup>O)<sub>2</sub>P-μO-P(OR<sup>F</sup>)<sub>2</sub> {R<sup>F</sup> = C(CF<sub>3</sub>)<sub>3</sub>} (**7**). Orthorhombic, Pbca, 110 K, R<sub>1</sub> = 0.1170, wR<sub>2</sub> = 0.3379. Extensive disorder (modelled over two positions) is present in the structure. Only one position is shown (and bond lengths and angles given for this) for clarity. Selected bond lengths (Å) and angles (°): P(1)-O(1) 1.589(9), P(1)-O(2) 1.637(9), P(1)-O(5) 1.63(5), P(2)-O(3) 1.611(8), P(2)-O(4) 1.643(9), P(2)-O(5) 1.62(4), P(1)-O(5)-P(2) 136(3), O(1)-P(1)-O(2) 93.6(4), O(1)-P(1)-O(5) 96(2), O(2)-P(1)-O(5) 96.2(9), O(3)-P(2)-O(4) 93.4(5), O(3)-P(2)-O(5) 101(2), O(4)-P(2)-O(5) 100.2(8).

### Steric properties

The steric properties of P(III) ligands are very important in coordination chemistry and catalysis. Establishing the steric parameters of ligands **1-6** is important for understanding their



relationship to more commonly encountered ligands. Tolman's cone angles ( $\theta$ ) and % buried volumes (% $V_{\text{bur}}$ ) have been chosen here to describe steric properties,<sup>[2a, 17]</sup> as they are available for many other ligand systems, hence wider comparison can be made, but also because some alternative steric parameters (i.e.  $S_4'$ ) are known to fail for phosphites. A ligand's cone angle can vary quite considerably depending on the metal fragment that it is attached to, as conformational flexibility allows some ligands to change their steric profile to respond to the steric requirements of other ligands at the metal center. As such, we have calculated  $\theta$  (see ESI for details) for **1-6** using structural data for a range of complexes (from both experimental and DFT studies). The range of  $\theta$  values observed for a particular ligand can be interpreted as an estimate of its conformational flexibility. The results are shown in Table 2, alongside data for some commonly encountered ligands for comparison and % $V_{\text{bur}}$  data for the same ligands.

**Table 2.** Ligand cone angles ( $\theta$  in  $^\circ$ ) and % buried volume data (% $V_{\text{bur}}$ ) for **1-6**. Where two ligands are present at the metal center,  $\theta$  for both ligands are reported.

Ligand	[Ni(CO) <sub>3</sub> L] <sup>[a]</sup>	[W(CO) <sub>5</sub> L] <sup>[a]</sup>	[Ru 1] <sup>[b]</sup>	[Ru 2] <sup>[c]</sup>	% $V_{\text{bur}}$
<b>1</b>	171	153	155	-	33.0 <sup>[d]</sup>
<b>2</b>	176	161	143	142	32.9 <sup>[d]</sup>
<b>3</b>	154	151	145	144	29.5 <sup>[d]</sup>
<b>4</b>	193	177	182	-	42.0 <sup>[d]</sup>
<b>5</b>	177	163	171	-	33.5 <sup>[d]</sup>
<b>6</b>	166	161	162	143	33.9 <sup>[d]</sup>
PMe <sub>3</sub>	118 <sup>[f]</sup>				22.2 <sup>[g]</sup>
P(CF <sub>3</sub> ) <sub>3</sub>	137 <sup>[f]</sup>				26.6 <sup>[h]</sup>
PPh <sub>3</sub>	145 <sup>[f]</sup>				29.6 <sup>[g]</sup>
P(OBu) <sub>3</sub>	175 <sup>[f]</sup>				28.4 <sup>[h]</sup>
PBu <sub>3</sub>	182 <sup>[f]</sup>				26.7 <sup>[g]</sup>
P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	184 <sup>[f]</sup>				37.3 <sup>[g]</sup>
PMes <sub>3</sub> <sup>[e]</sup>	212 <sup>[f]</sup>				47.6 <sup>[g]</sup>

[a] From optimised structures at the (RI-)BP86/SV(P) level. [b] From single-crystal X-ray diffraction studies of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2\text{L}][\text{PF}_6]$ . [c] From single-crystal X-ray diffraction studies of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2\text{L}_2][\text{PF}_6]$ . In the case of ligands **3** and **6** two independent complexes are present in the asymmetric unit and the average  $\theta$  values are reported. [d] Calculated from optimised structures of  $[\text{Ni}(\text{CO})_3\text{L}]$  with the M-P length set to 2.28 Å using the SambVca 2.0 package.<sup>[19]</sup> [e] Mes = 2, 4, 6 trimethylphenyl. [f] Taken from references<sup>[20]</sup>. [g] Taken from reference<sup>[17a]</sup>. [h] Calculated from optimised structures of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})\text{L}]$  with the M-P length set to 2.28 Å using the SambVca 2.0 package.<sup>[19]</sup>

The cone angles for  $[\text{Ni}(\text{CO})_3\text{L}]$  complexes of ligands **1-6** allow a comparison of their steric properties with a range of examples from the literature (Table 2). These data suggest that

ligands **1-6** are somewhat larger than  $\text{P}(\text{CF}_3)_3$  and  $\text{PPh}_3$  and have similar steric properties to the bulky ligands  $\text{P}(\text{Bu}^t)_3$ ,  $\text{P}(\text{C}_6\text{F}_5)_3$  and  $\text{P}(\text{OBu}^t)_3$ . However, the conformational flexibility of the  $-\text{C}_6\text{F}_5$  and  $-\text{OBu}^t$  groups in the latter may allow these ligands to change their steric profile quite dramatically depending on the requirements of a particular metal fragment, whereas significantly reduced conformational flexibility is expected with ligands such as **4**. As expected,  $\text{P}\{\text{OC}(\text{CF}_3)_3\}_3$  (**4**) shows a very large cone angle of  $193^\circ$  at  $\text{Ni}(\text{CO})_3$ , which is considerably larger than  $\text{P}(\text{Bu}^t)_3$  and even approaches the size of *ortho*-substituted aryl phosphines such as  $\text{PMes}_3$  ( $\theta = 212^\circ$ ). It has been found that cone angles and % buried volumes are strongly correlated for many metal-ligand combinations.<sup>[17a]</sup> However, % $V_{\text{bur}}$  places a greater emphasis on the steric properties proximal to the metal, whereas  $\theta$  includes steric effects at larger distances, which is important in some systems.<sup>[21]</sup> Consideration of the % $V_{\text{bur}}$  values in Table 2 confirms that **1-6** are large ligands, but highlights that most have relatively remote steric hindrance rather than the significant proximal steric profile presented by ligands such as  $\text{PMes}_3$ .

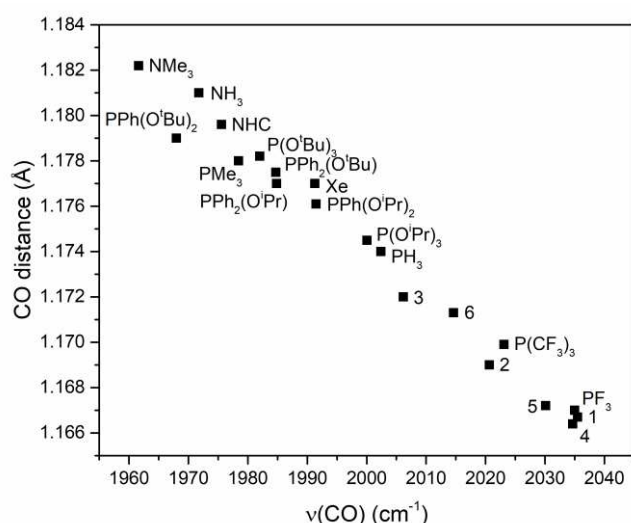
When cone angles for **1-6** from all available crystal structures/calculations are considered it is clear that **4** is consistently larger than the other ligands across a range of complexes. The bulky  $-\text{OC}(\text{CF}_3)_3$  groups are locked into one conformation in **4**, rather than exhibiting the multiple conformations often observed for phosphites, giving this ligand a relatively stable steric profile across a range of coordination environments. The phosphite **1** has a large cone angle for many complexes, but in the case of  $[\text{W}(\text{CO})_5\text{L}]$   $\theta$  is similar for **1** to other ligands with the  $-\text{OC}(\text{H})(\text{CF}_3)_2$  group. This may be an indication of conformational flexibility. Those ligands with  $-\text{OC}(\text{CF}_3)_3$  groups appear to be a little less flexible than those with  $-\text{OC}(\text{H})(\text{CF}_3)_2$  groups (based on their generally smaller range of  $\theta$  values). All ligands occupy the desired "bulky" region of ligand space and are comparable, or larger than recently reported  $\alpha$ -cationic phosphines.<sup>[7a]</sup>

### Electronic properties

The electronic properties of ligands have been assessed using a variety of methods, all of which have positive and negative aspects. A convenient approach, which we have used previously to assess the donor properties of very electron-rich ligands, has been proposed by Gusev *et al.*<sup>[3d, 22]</sup> This involves geometry optimizations and vibrational frequency analyses of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})\text{L}]$  complexes (where L is the desired ligand), using DFT methods to obtain CO stretching frequencies and C-O bond lengths that vary as a function of the donor/acceptor properties of L. The use of this complex, as opposed to other commonly used gauges of electronic properties {e.g.  $[\text{Ni}(\text{L})(\text{CO})_3]$ }, allows the comparison of a large range of different ligand classes using the same scale. It has been noted, however, that methods to assess ligand donor properties through  $\nu(\text{CO})$  in metal carbonyl complexes can be affected by intramolecular interactions between the ligands of interest and CO, which perturbs  $\nu(\text{CO})$ .<sup>[7a, 23]</sup> As such, cautious analysis of the data is advisable for larger ligands, where these interactions may be present. A plot of

$\nu(\text{CO})$  against CO bond length for a range of ligands including **1-6** is shown in Figure 5.

Strongly donating ligands, e.g.  $\text{PMe}_3$  appear at the top left of Figure 5, as these increase the extent of back bonding from Ir to the CO ligand. Electron-poor ligands, e.g.  $\text{PF}_3$ , appear at the bottom right of Figure 5, as they are more  $\pi$ -acidic and reduce the amount back bonding from the metal to CO.  $\text{PH}_3$  has electronic properties in-between these two extremes. Ligands **1** and **4** are found to have similar electronic properties to  $\text{PF}_3$ . Substituting fluorinated alkoxide groups for phenyl groups brings the ligands' electronic properties closer to  $\text{PH}_3$ . An interesting feature of these data is that although one would expect the perfluoro-*t*-butyl phosphite **4** to have greater  $\pi$ -acidity than **1**, due to the extra  $\text{CF}_3$  groups, the data suggest that the electronic properties of the two ligands are similar. This may be a consequence of the steric bulk of **2**, which prevents a close approach of the ligand to the metal center. This would reduce metal-phosphorus orbital overlap and prevent metal-ligand back donation. There is a slight elongation of the Ir-P bond in the optimized structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})(\textbf{4})]$  (2.198 Å) compared to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})(\textbf{1})]$  (2.194 Å) that may be related to this.



**Figure 5.** A plot of  $\nu(\text{CO})/\text{cm}^{-1}$  against CO bond length/Å for a range of ligands including **1-6**. NHC = 1,3-Dimethylimidazol-2-ylidene. Geometry optimisations and vibrational frequency calculations performed at the (RI)-BP86/SV(P) level.

In order to assess the electronic properties of these ligands via experimental measurements, tungsten and rhodium carbonyl complexes of **1-6** were prepared. Tungsten carbonyl complexes of the form  $[\text{W}(\text{CO})_5\text{L}]$ , where **L = 1-6** were prepared by reaction of  $[\text{W}(\text{CO})_5(\text{THF})]$  with the relevant ligand in tetrahydrofuran (THF) solution.<sup>[24]</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data for these complexes in THF, along with the carbonyl IR stretching frequencies (solution phase in THF/hexane) are summarized in Table 3. Four of these complexes were amenable to purification by sublimation (to remove excess  $[\text{W}(\text{CO})_6]$  present in the crude products). However, complexes involving ligands **4** and **5** consistently

decomposed under these conditions. It appears that ligand loss/exchange resulting in the formation of  $[\text{W}(\text{CO})_6]$  and unidentified tungsten containing species is facile for these ligands. EI-MS confirmed the presence of the tungsten pentacarbonyl-ligand complexes ( $[\text{M}]^+$  observed) in all cases and there is no evidence for the formation of  $[\text{W}(\text{CO})_4\text{L}_2]$ .

**Table 3.** Selected spectroscopic data for  $[\text{W}(\text{CO})_5\text{L}]$  complexes, where **L = 1-6**.

Ligand	$\delta$ ( $^{31}\text{P}\{^1\text{H}\}$ ) <sup>[a]</sup>	( $A_1$ ) <sub>1</sub> $\nu\text{CO}$ <sup>[b]</sup>	( $A_1$ ) <sub>2</sub> $\nu\text{CO}$ <sup>[b]</sup>	( $E$ ) $\nu\text{CO}$ <sup>[b]</sup>	( $B_1$ ) $\nu\text{CO}$ <sup>[b]</sup>
<b>1</b>	147 (452)	2097	2002	1975	2017
<b>2</b>	183 (357)	2088	1970	1962	2002
<b>3</b>	150 (291)	2080	1968	1953	1992
<b>4</b>	150 (292)	2097 <sup>[c]</sup>	1989 <sup>[c]</sup>	1976 <sup>[c]</sup>	2007 <sup>[c]</sup>
<b>5</b>	174 (374)	2089 <sup>[c]</sup>	1980 <sup>[c]</sup>	1967 <sup>[c]</sup>	1999 <sup>[c]</sup>
<b>6</b>	149 (304)	2081	1964	1954	1996
$\text{PF}_3$ <sup>[25]</sup>	121 (496)	2101	2005	1975	-
$\text{P}(\text{CF}_3)_3$ <sup>[26]</sup>	55 (300)	2101	2001	1989	-
$\text{P}(\text{OMe})_3$ <sup>[27]</sup>	138 (386)	2081	1952	1952	1980
$\text{P}(\text{OPr}^i)_3$ <sup>[27a, 28]</sup>	130 (381)	2075	1952	1937	-
$\text{PPh}_3$ <sup>[27b]</sup>	21 (243)	2075	1942	1942	1980
$\text{PMe}_3$ <sup>[26]</sup>	-40 (230)	2071	1949	1941	-

[a] Chemical shifts in ppm and coupling constants in Hz. [b] Stretching frequencies in  $\text{cm}^{-1}$ . Note that the antisymmetric ( $E$  and ( $A_1$ )<sub>2</sub>) stretches are greater in peak intensity, therefore are more easily identified in the IR spectrum. As such, the reported vibrational frequencies for these stretches may be more reliable.  $B_1$  symmetric stretches are observed for **1-6** as the ligands result in complexes without perfect  $C_{4v}$  symmetry. [c] IR data extrapolated from (RI)-BP86/SV(P) calculations (see ESI for details).

Both the IR stretching frequencies and  $^1J_{\text{WP}}$  coupling constants in these complexes can be used as indicators of the electronic properties of the ligands. The  $^1J_{\text{WP}}$  coupling constants appear to follow a trend where increasingly large values are seen for more electron-poor,  $\pi$ -acidic ligands. The  $^1J_{\text{WP}}$  values for **1-3** (452, 357 and 291 Hz respectively) follow a trend that fits with the expectation that increasing the number of fluorinated alkoxide groups at P increases the  $\pi$ -acceptor character of the ligand. Steric effects appear to have an influence on the  $^1J_{\text{WP}}$  coupling constants for ligands involving the bulky perfluorinated *t*-butoxy groups, as a simple relationship between  $^1J_{\text{WP}}$  and the number of alkoxy groups at P is not found for **4-6** ( $^1J_{\text{WP}} = 292$ , 374 and 304 Hz respectively). As observed with the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})\text{L}]$  stretching frequencies, the perfluorinated *t*-butyl phosphite **4** appears less  $\pi$ -acidic than would be expected given the number of fluorinated substituents. The steric bulk of **4** presumably prevents a close approach to the metal and this effect appears to be more pronounced for  $[\text{W}(\text{CO})_5\text{L}]$  complexes,

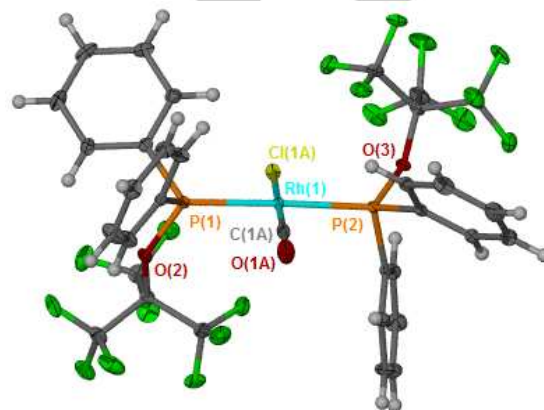
due to the larger steric requirements of the  $\text{W}(\text{CO})_5$  fragment. When the  $^1J_{\text{WP}}$  data for  $[\text{W}(\text{CO})_5\text{L}]$  complexes involving **1-6** are compared to some common ligands in the literature the similarity in electronic properties between  $\text{PF}_3$  and **1** are again evident (496 vs. 452 Hz respectively). The other ligands span a range of  $^1J_{\text{WP}}$  values that place their electronic properties between those of  $\text{P}(\text{CF}_3)_3$  and non-fluorinated phosphites at this metal fragment, consistent with their occupation of the electron-poor region of ligand space.

The CO stretching frequencies for these tungsten complexes also show a trend of increasing  $\pi$ -acidity when more fluorinated alkoxy groups are substituted on the P(III) ligands. For example, the antisymmetric *E* stretch moves to lower wavenumbers from **1-3** (1975, 1962, 1953  $\text{cm}^{-1}$  respectively) and from **4-6** (1976, 1967, 1954  $\text{cm}^{-1}$  respectively). These data are similar for the related  $-\text{OC}(\text{H})(\text{CF}_3)_2$  and  $-\text{OC}(\text{CF}_3)_3$  substituted ligands, presumably due to steric effects. When compared to ligands in the literature, the CO stretching frequencies agree with the trends seen in the tungsten-phosphorus ( $^1J_{\text{WP}}$ ) coupling constants in most cases, but there are some subtle differences. For example, the similarity between **1** and  $\text{PF}_3$  is still evident {e.g. (E)  $\nu(\text{CO}) = 1975 \text{ cm}^{-1}$  for both}. However, the relative ordering of ligands **1-6** compared to  $\text{P}(\text{CF}_3)_3$  and the non-fluorinated phosphites is different to that suggested by the  $^1J_{\text{WP}}$  data {with  $\text{P}(\text{CF}_3)_3$  appearing to be the best acceptor ligand and ligands **1-6** showing better  $\pi$ -acceptor properties (i.e.  $\nu\text{CO}$  at higher wavenumbers) than the non-fluorinated phosphites}. This highlights the complexities involved in determining the relative electronic properties of different ligands and is a reminder that an electronic scale based on a single-property may not give a complete picture. In fact, a ligand's steric and electronic properties are probably best assessed in a range of different situations using several descriptors.

### Coordination chemistry

Unfortunately it was not possible to grow crystals of  $[\text{W}(\text{CO})_5\text{L}]$  (**L = 1-6**) complexes that were suitable for X-ray structural analysis. This is hampered in part by the slow decomposition of all complexes, even at  $-20^\circ\text{C}$  under an inert atmosphere. However, Itami *et al.* have reported Rh complexes of the form  $[\text{trans-RhCl}(\text{CO})(\text{L})_2]$  where **L = 1** and **2** and explored their application in catalytic C-C bond forming reactions.<sup>[18]</sup> In order to make some comparisons across a range of ligand types we have synthesized analogous complexes where **L = 4, 5** and **6** by reaction of  $[\text{RhCl}(\text{CO})_2]_2$  with two equivalents of the free ligands in  $\text{CD}_2\text{Cl}_2$ . In the case of  $[\text{trans-RhCl}(\text{CO})(\text{6})_2]$  (**8**), crystals suitable for single-crystal X-ray diffraction studies were obtained and the structure of this complex is shown in Figure 6. The complex shows a slightly distorted square planar geometry around Rh, with relatively short Rh-P distances (2.287 and 2.302, av. 2.295 Å), which are significantly shorter than the average Rh-P distance (2.328 Å) for  $[\text{trans-RhCl}(\text{CO})(\text{PR}_3)_2]$  complexes (with  $R_1 < 0.1$ ) in the Cambridge Structural Database (CSD).<sup>[29]</sup> This may be a structural indication of increased  $\pi$ -back donation from Rh to this relatively electron-poor ligand. The observation of even shorter Rh-P distances (2.2597(8) and 2.2550(7), av. 2.257 Å) in the  $\text{trans-RhCl}(\text{CO})(\text{L})_2$  complex of the more

electron-poor ligand **1**, support this suggestion. The  $[\text{trans-RhCl}(\text{CO})(\text{L})_2]$  complexes of **1, 2, 4, 5** and **6** from this work and that of Itami *et al.* also allow a comparison of donor properties across the series using  $\nu(\text{CO})$  and  $^1J_{\text{RhP}}$  data in a similar way to the Ir and W complexes described above. As this shows similar features to the data discussed for the Ir and W species a summary of key data is included in the ESI.



**Figure 6.** Single-crystal X-ray structure of  $\text{RhCl}(\text{CO})(\text{PPh}_2\text{OR}^{\text{F}})_2$  (**8**), where  $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$ . Tetragonal,  $\text{P4}_2/\text{n}$ , 110 K,  $R_1 = 0.0306$ ,  $wR_2 = 0.0645$ . Cl and CO positions are disordered, disordered parts omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles ( $^\circ$ ):  $\text{Rh}(1)-\text{P}(1) = 2.2866(4)$ ,  $\text{Rh}(1)-\text{P}(2) = 2.3017(4)$ ,  $\text{Rh}(1)-\text{Cl}(1\text{A}) = 2.381(1)$ ,  $\text{Rh}(1)-\text{C}(1\text{A}) = 1.779(8)$ ,  $\text{C}(1\text{A})-\text{O}(1\text{A}) = 1.15(1)$ ,  $\text{P}(1)-\text{Rh}-\text{P}(2) = 177.96(2)$ ,  $\text{C}(1\text{A})-\text{Rh}-\text{Cl}(1\text{A}) = 169.68(5)$ ,  $\text{P}(1)-\text{Rh}(1)-\text{Cl}(1\text{A}) = 92.34(3)$ ,  $\text{P}(2)-\text{Rh}(1)-\text{Cl}(1\text{A}) = 87.22(3)$ ,  $\text{C}(1\text{A})-\text{Rh}(1)-\text{P}(1) = 88.7(1)$ ,  $\text{C}(1\text{A})-\text{Rh}(1)-\text{P}(2) = 91.62(14)$ . No clathrate-type solvates, as seen in a recent related study, were found for any complex.<sup>[30]</sup>

In addition to the W and Rh complexes described above, Ru complexes of the form  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_{3-n}(\text{L})_n][\text{PF}_6]$ , where **L = 1-6** and  $n = 1$  or 2, have been synthesized by reaction of the free ligand in the relevant stoichiometry with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_3][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$ . Ru complexes of this type are of relevance in a range of catalytic transformations including alkyne dimerisation, alkyne hydration etc.<sup>[31]</sup> The spectroscopic data for these complexes are presented in Table 5. In all cases it was possible to obtain crystals suitable for analysis by single-crystal X-ray diffraction studies by slow diffusion of hexane into a solution of the complex in  $\text{CH}_2\text{Cl}_2$  at room temperature. Representative structures of  $n = 1$  and  $n = 2$  complexes are shown in Figure 7 and 8 respectively and a .cif file containing all structures is included as supporting information.

In all structurally characterized  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_{3-n}(\text{L})_n][\text{PF}_6]$  (**L = 1-6**,  $n = 1, 2$ ) complexes Ru is found to adopt a distorted tetrahedral geometry (if the centroid of the  $\text{C}_5\text{H}_5$  ring is taken as one vertex). The phosphite, phosphonite and phosphinite ligands in these complexes show a variety of conformations, due to rotation around the P-O bond, in the different structures. In the majority of cases the oxygen lone pairs on the  $\text{OR}^{\text{F}}$  group(s) point either towards the metal or broadly perpendicular to the M-P bond, which has the effect of moving the  $\text{R}^{\text{F}}$  group(s) away from the metal. This presumably



reduces steric repulsion between the  $R^F$  groups and other ligands. Interestingly, in all ruthenium complexes of ligands containing the  $-C(H)(CF_3)_2$  group the  $^{19}F$  NMR spectra show two signals relating to inequivalent  $CF_3$  environments. This suggests that coordination restricts rotation around the P-O or C-O bonds at room temperature on the NMR timescale, resulting in atropisomerism (atropisomers are only observed in the free ligands for ligand **2**, *vide supra*).

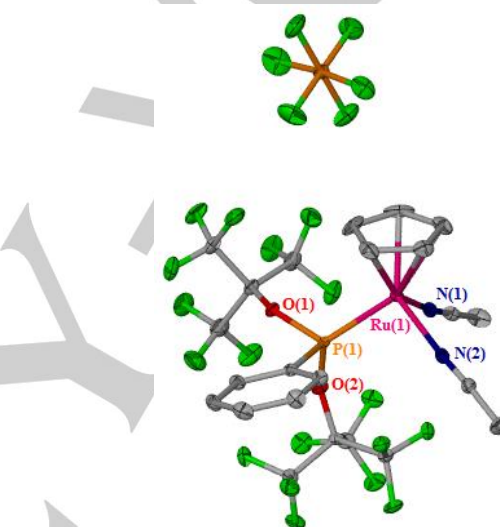
**Table 5.** Spectroscopic and structural data for  $[(\eta^5-C_5H_5)Ru(NCMe)_3-n(L)_n][PF_6]$  complexes, where  $L = 1-6$  and  $n = 1$  or  $2$ .

Ligand (L)	$\delta^{31}P$	$\delta^{19}F$ [a]	Ru-P(1)	Ru-P(2)	Ru-N(1)	Ru-N(2)
<b>1</b> , $n = 1$ ( <b>9</b> ) <sup>[b]</sup>	162	-73.8, -74.0	2.206	-	2.05	2.05
<b>1</b> , $n = 2$ [c]			-	-	-	-
<b>2</b> , $n = 1$ ( <b>10</b> )	199	-73.4, -73.6	2.224	-	2.061	2.065
<b>2</b> , $n = 2$ ( <b>11</b> )	199	-73.2, -73.4	2.262	2.265	2.059	-
<b>3</b> , $n = 1$ ( <b>12</b> )	172	-72.6, -72.8	2.264	-	2.059	2.054
<b>3</b> , $n = 2$ ( <b>13</b> )	168	-72.4, -72.7	2.278	2.277	2.046	-
<b>4</b> , $n = 1$ ( <b>14</b> )	117	-71.0	2.233	-	2.015	2.071
<b>4</b> , $n = 2$ [c]	-	-	-	-	-	-
<b>5</b> , $n = 1$ ( <b>15</b> )	192	-70.5	2.254	-	2.047	2.061
<b>5</b> , $n = 2$ [c]	-	-	-	-	-	-
<b>6</b> , $n = 1$ ( <b>16</b> )	167	-70.4	2.263	-	2.069	2.065
<b>6</b> , $n = 2$ ( <b>17</b> )	185	-69.1	2.289	2.299	2.048	-

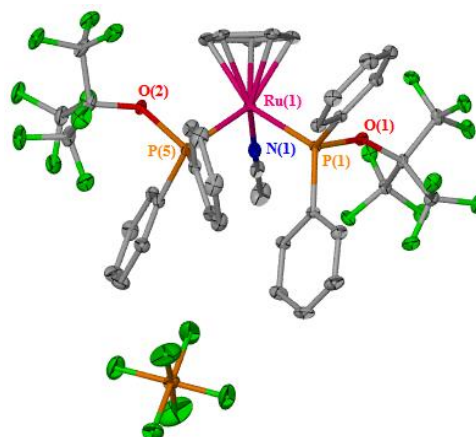
[a] Two environments are observed for each  $C(H)(CF_3)_2$  group in the  $^{19}F$  NMR of complexes containing this functional group, due to atropisomerism. [b] There is significant disorder present in this structure (for  $C_5H_5$ ,  $[PF_6]^-$ ), which resulted in a relatively poor data set compared to other Ru complexes. [c] We found no evidence of the formation of these species in solution NMR spectroscopic studies. In **13**, two molecules of  $CH_2Cl_2$  and in **17** one molecule of  $CH_2Cl_2$  of crystallization were found in the asymmetric units. No clathrate-type solvates, as seen in a recent related study, were found for any complex.<sup>[30]</sup>

The Ru-P distances in these complexes appear to follow a trend based on the  $\pi$ -acidity of the P-ligand(s) and the number of P-ligands at Ru. In general the Ru-P distances are shortest for the most  $\pi$ -acidic ligands for each type of alkoxide substituent  $\{O(H)(CF_3)_2$  and  $OC(CF_3)_3\}$ . This can be interpreted as being due to an increase in  $\pi$ -backdonation from Ru to the more electron-poor ligands, which strengthens the Ru-P bond. For example, where  $R^F = O(H)(CF_3)_2$  and  $n = 1$  a very short Ru-P bond is seen for the phosphite **1** (2.206 Å) whereas a significantly longer Ru-P bond is seen for the phosphinite **3** (2.264 Å). A similar trend of increasing Ru-P bond length with decreasing  $\pi$ -acidity of the P-ligand is also seen where  $R^F =$

$OC(CF_3)_3$  and  $n = 1$ . However, it is interesting to note that the Ru-P bond in the Ru-complex of phosphite **4** (2.233 Å) is significantly longer than that seen in the hexafluoroisopropyl-substituted analogue (complex **9**, Ru-P = 2.206 Å), presumably due to the much larger steric profile of **4**. When comparing complexes of the same ligand with  $n = 1$  and  $n = 2$  (only complexes **12** and **13** allow this from the available data) it appears that increasing the number of P-ligands at Ru leads to an increase in the R-P bond lengths (from 2.264 to 2.278 Å in the case of **12** and **13**). This may be a result of competition between the P-ligands for  $\pi$ -backdonation from Ru or simply due to steric repulsion between these relatively large ligands.



**Figure 7.** Single-crystal X-ray structure of  $[(\eta^5-C_5H_5)Ru(NCMe)_2[PPh(OC(CF_3)_3)_2]][PF_6]$ , **17**. Monoclinic,  $P2_1/c$ ,  $R_1 = 0.0401$ ,  $wR_2 = 0.0833$ . Hydrogen atoms and disordered parts (of  $[PF_6]^-$  anion) omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles ( $^\circ$ ): Ru(1)-P(1) = 2.2541(6), Ru(1)-N(1) = 2.047(2), Ru(1)-N(2) = 2.061(2), N(1)-Ru(1)-P(1) = 94.77(6), N(2)-Ru(1)-P(1) = 97.49(6), N(1)-Ru(1)-N(2) = 86.63(8), O(1)-P(1)-O(2) = 94.10(9).





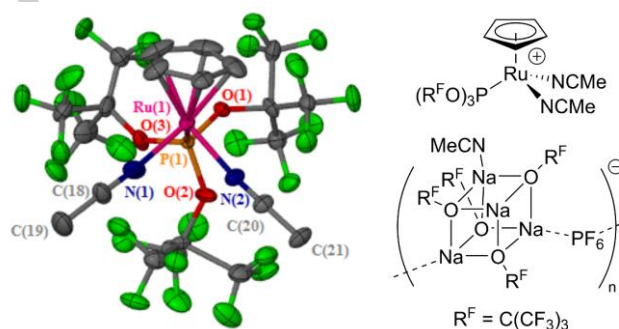
**Figure 8.** Single-crystal X-ray structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})\{\text{PPh}_2(\text{OC}(\text{CF}_3)_3)\}][\text{PF}_6] \cdot 0.5\text{CH}_2\text{Cl}_2$ , **17**. Monoclinic,  $P2_1$ ,  $R_1 = 0.0332$ ,  $wR_2 = 0.0745$ . The asymmetric unit contains two ion pairs, only one of which is shown for clarity. Hydrogen atoms and solvent of crystallisation omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles (°): Ru(1)-P(1) = 2.2881(9), Ru(1)-P(2) = 2.2988(7), Ru(1)-N(1) = 2.048(2), N(1)-Ru(1)-P(1) = 89.96(7), N(1)-Ru(1)-P(2) = 96.01(6), P(1)-Ru(1)-P(2) = 99.07(3).

When compared to structural data in the literature, it was found that complexes **9–17** have Ru-P bond lengths that are significantly shorter than the average Ru-P distances for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})(\text{L})_2]^+$  (where L = any P(III) ligand) salts reported in the CSD (av. Ru-P = 2.33 Å for > 180 structures with  $R_1 < 0.1$ ). Indeed, complex **9** shows the shortest Ru-P distance for any analogous complex with  $n = 1$  or 2. The shortest Ru-P distance previously reported was 2.231(2) Å.<sup>[32]</sup> The Ru-N distances are, in most cases, relatively insensitive to the other ligands at Ru.

The solution chemistry in this system for the very bulky phosphite **4** is more complex than for the other ligands. Evidence for the formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2(\text{P}(\text{OC}(\text{CF}_3)_3)_3)][\text{PF}_6]$  (**14**) was found in the  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectra with the appearance of signals at 117 and -71.1 ppm respectively after addition of a  $\text{CH}_2\text{Cl}_2$  solution of **4** to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_3][\text{PF}_6]$ . These were accompanied by the observation of free MeCN (at  $\delta = 2.10$  ppm) in the  $^1\text{H}$  NMR spectrum. However, even after 4 days of stirring at room temperature ligand exchange is incomplete, with free **4** being seen in the  $^{31}\text{P}$  NMR spectrum and a significant quantity of colorless crystalline material (undissolved **4**, which is relatively poorly soluble) seen in the reaction vessel. Heating the reaction mixture at 43 °C for 24 hours in an attempt to solubilize ligand **4** and facilitate ligand exchange resulted in a decrease in the intensity of signals for **14** in the NMR spectra and a new species with  $\delta(^{31}\text{P}) = 120.7$  (doublet of multiplets,  $^1J_{\text{PF}} = 1252$  Hz). This was assigned as the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2(\text{PF}(\text{OC}(\text{CF}_3)_3)_2)][\text{PF}_5\{\text{OC}(\text{CF}_3)_3\}]$  (**19**), which is supported by ESI-MS data which showed a strong signal at 768.9  $m/z$  (for  $[\text{M}]^+$ ) in the positive mode and 576.9  $m/z$  (for  $[\text{PF}_5\{\text{OC}(\text{CF}_3)_3\}]^-$ ) in the negative mode.  $^{19}\text{F}$  NMR data also suggest the presence of this anion  $\delta(^{19}\text{F}) = -62.3$  ( $F_{\text{equatorial}}$ , doublet of doublet of multiplets,  $^1J_{\text{PF}} = 746$  Hz,  $^2J_{\text{FF}} = 50$  Hz) -73.86 ( $F_{\text{axial}}$ , doublet of quintets,  $^1J_{\text{PF}} = 700$  Hz,  $^2J_{\text{FF}} = 50$  Hz) and the P-F group on the substituted ligand  $\delta(^{19}\text{F}) = 1.25$  (doublet of multiplets,  $^1J_{\text{PF}} = 1252$  Hz,  $^4J_{\text{FF}} = 4$  Hz) ppm. The mechanism for this fluoride-alkoxide group exchange between ligand **4** and the  $[\text{PF}_6]^-$  anion is unclear, but the driving force is likely to be reduction of the steric bulk of the ligand and so formation of a less sterically congested complex.

Although the reaction of **4** with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_3][\text{PF}_6]$  does not proceed to completion at room temperature, it was possible to identify crystals containing the desired cation (**14**), after decanting to remove unreacted **4** and crystallisation from a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$ . The molecular structure of **14** is shown in Figure 9. While this contains the desired cation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2(\text{P}(\text{OC}(\text{CF}_3)_3)_3)]^+$ , in **14** it crystallises as a salt with the unusual counterion  $[\text{Na}_4\{\text{OC}(\text{CF}_3)_3\}_4\text{PF}_6 \cdot \text{MeCN}]^-$ . This anion results from the coordination of a  $[\text{PF}_6]^-$  anion and a

molecule of MeCN to a neutral sodium alkoxide cluster  $[\text{Na}_4\{\text{OC}(\text{CF}_3)_3\}_4]$ , which was present as a low concentration impurity in the sample of **4** used in this reaction. Cubic clusters are common structural forms in alkoxides of this type.<sup>[33]</sup> To the best of our knowledge compound **14** is the first structurally characterized example of a metal complex of **4**. The basic structure of **14** is similar to the other complexes described above. However, given the size of this ligand, the remarkably short Ru-P bond length (2.233 Å) is particularly noteworthy and may be an indication of relatively strong  $\pi$ -backdonation from Ru to P. Another interesting feature is the marked asymmetry in the Ru-N bond lengths (2.015 and 2.071 Å), which appear in other complexes described here to be relatively insensitive to the nature of the ligand. Although the ligand is heavily disordered (by rotation of  $\text{CF}_3$  groups in the  $-\text{C}(\text{CF}_3)_3$  groups) it appears that there is a closer approach of one C-F bond from **4** to the C $\equiv$ N bond of the coordinated MeCN that displays a particularly short Ru-N distance (2.015 Å). It is possible that this asymmetry in the weak intramolecular interactions in the solid-state structure of **14** results in the asymmetry observed in the Ru-N bond distances, rather than this being related to the nature of the metal to P-ligand interaction.



**Figure 9.** Single-crystal X-ray structure of the cation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{NCMe})_2(\text{P}(\text{OC}(\text{CF}_3)_3)_3)][\text{Na}_4(\text{OR}^{\text{F}})_4\text{PF}_6 \cdot \text{MeCN}]$ , **14**, alongside the Lewis structures of both ions for clarity. Monoclinic,  $P2_1/n$ ,  $R_1 = 0.0623$ ,  $wR_2 = 0.1677$ . Hydrogen atoms, anion and disordered parts (the  $\text{C}_4\text{F}_9$  groups of both the anion and cation are heavily disordered by  $\text{CF}_3$  group rotation) omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles (°): Ru(1)-P(1) = 2.233(1), Ru(1)-N(1) = 2.015(5), Ru(1)-N(2) = 2.071(4), N(1)-Ru(1)-P(1) = 94.00(13), N(2)-Ru(1)-P(1) = 93.18(10), N(1)-Ru(1)-N(2) = 86.70(17), O(1)-P(1)-O(2) = 98.4(3), O(1)-P(1)-O(3) = 97.8(3), O(2)-P(1)-O(3) = 96.2(4).

## Conclusions

The steric profiles, electronic properties and coordination chemistry of a range of phosphorus(III) ligands bearing highly fluorinated alkoxide substituents have been investigated using a range of experimental and computational approaches. These ligands are relatively easy to synthesize and their steric and electronic properties are tunable depending on the substituents present at the phosphorus center. All ligands occupy the bulky, electron-poor region of ligand space where there are currently relatively few ligands available. Coordination of these ligands to

a range of metal centers of relevance in homogeneous catalysis is possible and suggests that there are a range of potential applications of this class of ligand.

## Experimental Section

All air-sensitive experimental procedures were performed under an inert atmosphere of nitrogen, using standard Schlenk line and glovebox techniques. Dichloromethane and hexane were purified with the aid of an Innovative Technologies anhydrous solvent engineering system. Diethylether and tetrahydrofuran were dried over sodium and distilled and stored under N<sub>2</sub> prior to use. CD<sub>2</sub>Cl<sub>2</sub> used for NMR experiments was dried over CaH<sub>2</sub> and degassed with three freeze-pump-thaw cycles. CDCl<sub>3</sub> was dried over 4 Å molecular sieves, distilled and stored under N<sub>2</sub> prior to use. All reagents were purchased from commercial sources, unless their preparation is described in the ESI. Solid reagents were used in the glove box without further purification. Fluorinated alcohols were dried using 4 Å molecular sieves, distilled and stored under N<sub>2</sub> before use.

NMR spectra were acquired on a Jeol ECX-400 (Operating frequencies <sup>1</sup>H 399.78 MHz, <sup>31</sup>P 161.83 MHz, <sup>19</sup>F 376.17 MHz, <sup>13</sup>C 100.53 MHz) or a Bruker AVANCE 500 (Operating frequencies <sup>1</sup>H 500.13 MHz, <sup>31</sup>P 202.47 MHz, <sup>13</sup>C 125.77 MHz). <sup>31</sup>P and <sup>13</sup>C spectra were recorded with proton decoupling. Mass spectra were recorded on a Bruker micrOTOF or Esquire 6000 using electrospray ionisation. Infrared (IR) spectra were recorded on a Thermo-Nicolet Avator 370 FTIR spectrometer using CsCl solution cells for sample insertion at ca. 200 mg/mL concentration. A Unicam RS 10000E FTIR instrument, averaging 16 scans at resolution 1 cm<sup>-1</sup>, was used with a SensIR ATR-IR accessory for solid samples.

Geometry optimisations and vibrational frequency analyses were performed at the (RI)-BP86/SV(P) level with the full ligand substituents used in the experimental study using TURBOMOLE.<sup>[34]</sup>

Full details of all synthetic, spectroscopic and computational procedures are given in the ESI.

## Acknowledgements

We gratefully acknowledge the University of York and the EPSRC (DTA award to SH) for funding. We would also like to thank Professor Robin Perutz and Dr Jason Lynam for valuable discussions.

**Keywords:** Phosphorus ligands • coordination chemistry • ligand design • catalysis • DFT

- [1] A. G. Orpen, N. G. Connelly, *Organometallics* **1990**, *9*, 1206-1210.
- [2] a) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348; b) B. J. Dunne, R. B. Morris, A. G. Orpen, *J. Chem. Soc., Dalton Trans.* **1991**, 653-661; c) T. L. Brown, K. J. Lee, *Coord. Chem. Rev.* **1993**, *128*, 89-116; d) D. White, N. J. Coville, *Adv. Organomet. Chem.* **1994**, *36*, 95-158; e) K. A. Bunten, L. Z. Chen, A. L. Fernandez, A. J. Poe, *Coord. Chem. Rev.* **2002**, *233*, 41-51; f) K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **2003**, *125*, 4318-4324; g) I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991-3999; h) N. Fey, A. C. Tsipis, S. E. Harris, J. N. Harvey, A. G. Orpen, R. A. Mansson, *Chem. Eur. J.* **2006**, *12*, 291-302; i) N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704-722.
- [3] a) L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806-5811; b) C. H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573-1578; c) O. Kuhl, *Coord. Chem. Rev.* **2005**, *249*, 693-704; d) D. G. Gusev, *Organometallics* **2009**, *28*, 763-770; e) D. Cremer, E. Kraka, *Dalton Trans.* **2017**, *46*, 8323-8338; f) Q. Shi, R. J. Thatcher, J. Slattery, P. S. Sauari, A. C. Whitwood, P. C. McGowan, R. E. Douthwaite, *Chem. Eur. J.* **2009**, *15*, 11346-11360; g) J. Slattery, R. J. Thatcher, Q. Shi, R. E. Douthwaite, *Pure Appl. Chem.* **2010**, *82*, 1663-1671; h) R. J. Thatcher, D. G. Johnson, J. M. Slattery, R. E. Douthwaite, *Chem. Eur. J.* **2012**, *18*, 4329-4336.
- [4] a) R. A. Mansson, A. H. Welsh, N. Fey, A. G. Orpen, *J. Chem. Inf. Model.* **2006**, *46*, 2591-2600; b) N. Fey, J. N. Harvey, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne, M. Purdie, *Organometallics* **2008**, *27*, 1372-1383; c) N. Fey, M. F. Haddow, J. N. Harvey, C. L. McMullin, A. G. Orpen, *Dalton Trans.* **2009**, 8183-8196; d) J. Jover, N. Fey, J. N. Harvey, G. C. Lloyd-Jones, A. G. Orpen, G. J. Owen-Smith, P. Murray, D. R. J. Hose, R. Osborne, M. Purdie, *Organometallics* **2010**, *29*, 6245-6258; e) J. Jover, N. Fey, J. N. Harvey, G. C. Lloyd-Jones, A. G. Orpen, G. J. J. Owen-Smith, P. Murray, D. R. J. Hose, R. Osborne, M. Purdie, *Organometallics* **2012**, *31*, 5302-5306; f) N. Fey, S. Papadoulis, P. G. Pringle, A. Ficks, J. T. Fleming, L. J. Higham, J. F. Wallis, D. Carmichael, N. Mezailles, C. Muller, *Phosphorus Sulfur Silicon Relat. Elem.* **2015**, *190*, 706-714.
- [5] a) N. S. Imyanitov, G. I. Shmelev, *Zh. Obshch. Khim.* **1987**, *57*, 2161-2167; b) H. G. Ang, G. Manoussakis, Y. O. El-Nigumi, *J. Inorg. Nucl. Chem.* **1968**, *30*, 1715-1717; c) K. K. Banger, A. K. Brisdon, C. J. Herbert, H. A. Ghaba, I. S. Tidmarsh, *J. Fluorine Chem.* **2009**, *130*, 1117-1129; d) N. A. Barnes, A. K. Brisdon, F. R. William Brown, W. I. Cross, I. R. Crossley, C. Fish, C. J. Herbert, R. G. Pritchard, J. E. Warren, *Dalton Trans.* **2011**, *40*, 1743-1750; e) A. K. Brisdon, C. J. Herbert, *Chem. Commun. (Cambridge, U. K.)* **2009**, 6658-6660; f) Y. O. El Nigumi, H. J. Emeleus, *J. Inorg. Nucl. Chem.* **1970**, *32*, 3211-3212; g) B. N. Ghose, *J. Indian Chem. Soc.* **1978**, *55*, 1254-1259; h) J. Grobe, V. D. Le, *Chem. Ber.* **1990**, *123*, 1047-1049; i) M. Kato, K. Akiyama, M. Yamabe, *Asahi Garasu Kenkyu Hokoku* **1982**, *32*, 117-128; j) M. Kato, M. Yamabe, *J. Chem. Soc., Chem. Commun.* **1981**, 1173-1174; k) S.-i. Kawaguchi, Y. Minamida, T. Ohe, A. Nomoto, M. Sonoda, A. Ogawa, *Angew. Chem., Int. Ed.* **2013**, *52*, 1748-1752; l) L. C. Lewis-Alleyne, M. B. Murphy-Jolly, X. F. Le Goff, A. J. M. Cafyn, *Dalton Trans.* **2010**, *39*, 1198-1200; m) K. G. Sharp, I. Schwager, *Inorg. Chem.* **1976**, *15*, 1697-1701; n) Y. Sato, S.-i. Kawaguchi, A. Ogawa, *Chem. Commun. (Cambridge, U. K.)* **2015**, *51*, 10385-10388.
- [6] a) E. A. Allan, L. W. Reeves, *J. Phys. Chem.* **1963**, *67*, 591-594; b) K. K. Banger, R. P. Banham, A. K. Brisdon, W. I. Cross, G. Damant, S. Parsons, R. G. Pritchard, A. Sousa-Pedraes, *J. Chem. Soc., Dalton Trans.* **1999**, 427-434; c) N. A. Barnes, A. K. Brisdon, F. R. W. Brown, W. I. Cross, I. R. Crossley, C. Fish, J. V. Morey, R. G. Pritchard, L. Sekhri, *New J. Chem.* **2004**, *28*, 828-837; d) N. A. Barnes, A. K. Brisdon, F. R. W. Brown, W. I. Cross, C. J. Herbert, R. G. Pritchard, G. Sadiq, *Dalton Trans.* **2008**, 101-114; e) N. A. Barnes, A. K. Brisdon, M. J. Ellis, R. G. Pritchard, *J. Fluorine Chem.* **2001**, *112*, 35-45; f) N. A. Barnes, A. K. Brisdon, J. G. Fay, R. G. Pritchard, J. E. Warren, *Inorg. Chim. Acta* **2005**, *358*, 2543-2548; g) N. A. Barnes, A. K. Brisdon, C. Fish, J. V. Morey, R. G. Pritchard, J. E. Warren, *J. Fluorine Chem.* **2010**, *131*, 1156-1164; h) N. A. Barnes, A. K. Brisdon, M. Nieuwenhuyzen, R. G. Pritchard, G. C. Saunders, *J. Fluorine Chem.* **2007**, *128*, 943-951; i) A. H. Cowley, M. W. Taylor, *J. Amer. Chem. Soc.* **1969**, *91*, 1922-1933; j) S. S. Dubov, F. N. Chelobov, R. N. Sterlin, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 585; k) S. S. Dubov, B. I. Tetel'baum, R. N. Sterlin, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 691-692; l) H. G. Horn, R. Koentges, F. Kolkman, H. C. Marsmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1422-1426; m) H. G. Horn, F. Kolkman, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1427-1429; n) Y. Y. Kharitonov, C. Ni, A. V. Babaeva, *Zh. Neorg. Khim.* **1962**, *7*, 21-33; o) R. G. Peters, J. D. Palcio, R. G. Baughman, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, m1198-m1200; p) R. N. Sterlin, S. S. Dubov, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 117-118; q) R. N. Sterlin, S. S. Dubov, W.-K. Li, L. P. Vakhomchik, I. L. Knunyants, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1961**, *6*, 110-111; r) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, I. L. Khunyants, *Khim. Nauka Prom-st.* **1959**, *4*, 810-811; s) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 1991-1997.
- [7] a) M. Alcarazo, *Acc. Chem. Res.* **2016**, *49*, 1797-1805; b) K. Schwedtmann, G. Zanon, J. J. Weigand, *Chem. Asian J.* **2018**, *13*, 1388-1405; c) A. G. Barrado, J. M. Bayne, T. C. Johnstone, C. W. Lehmann, D. W. Stephan, M. Alcarazo, *Dalton Trans.* **2017**, *46*, 16216-16227; d) Y. Garcia-Rodeja, I. Fernandez, *Organometallics* **2017**, *36*, 460-466; e) E. Gonzalez-Fernandez, L. D. M. Nicholls, L. D. Schaaf, C. Fares, C. W. Lehmann, M. Alcarazo, *J. Am. Chem. Soc.* **2017**, *139*,

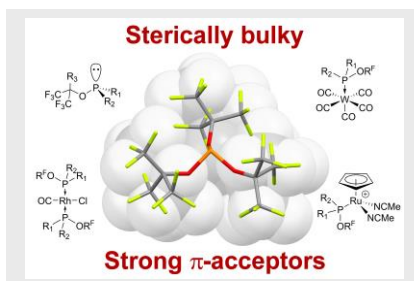
- 1428-1431; f) L. H. Gu, L. M. Wolf, A. Zielinski, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2017**, *139*, 4948-4953; g) M. Mehta, T. C. Johnstone, J. Lam, B. Bagh, A. Hermannsdorfer, M. Driess, D. W. Stephan, *Dalton Trans.* **2017**, *46*, 14149-14157; h) L. C. Wilkins, R. L. Melen, J. A. Platts, P. D. Newman, *Dalton Trans.* **2017**, *46*, 14234-14243; i) K. Abe, M. Kitamura, H. Fujita, M. Kunishima, *Molecular Catalysis* **2018**, *445*, 87-93; j) J. F. Binder, S. C. Kosnik, C. L. B. Macdonald, *Chem. Eur. J.* **2018**, *24*, 3556-3565; k) L. H. Gu, L. M. Wolf, W. Thiel, C. W. Lehmann, M. Alcarazo, *Organometallics* **2018**, *37*, 665-672; l) L. D. M. Nicholls, M. Marx, T. Hartung, E. Gonzalez-Fernandez, C. Golz, M. Alcarazo, *Acc. Catal.* **2018**, *8*, 6079-6085; m) N. Kuhn, J. Fahl, D. Blaser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729-734; n) D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* **2001**, *630*, 177-184; o) J. Y. Li, J. J. Peng, Y. Bai, G. D. Zhang, G. Q. Lai, X. N. Li, *J. Organomet. Chem.* **2010**, *695*, 431-436; p) J. Petuskova, H. Bruns, M. Alcarazo, *Angew. Chem. Int. Ed.* **2011**, *50*, 3799-3802; q) J. Petuskova, M. Patil, S. Holle, C. W. Lehmann, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2011**, *133*, 20758-20760; r) C. Maaliki, C. Lepetit, Y. Canac, C. Bijani, C. Duhayon, R. Chauvin, *Chem. Eur. J.* **2012**, *18*, 7705-7714; s) M. Alcarazo, *Chem. Eur. J.* **2014**, *20*, 7868-7877; t) A. Kozma, T. Deden, J. Carreras, C. Wille, J. Petuskova, J. Rust, M. Alcarazo, *Chem. Eur. J.* **2014**, *20*, 2208-2214; u) H. Tinnermann, C. Wille, M. Alcarazo, *Angew. Chem. Int. Ed.* **2014**, *53*, 8732-8736; v) I. Abdellah, Y. Canac, C. D. Mboyi, C. Duhayon, R. Chauvin, *J. Organomet. Chem.* **2015**, *776*, 149-152; w) C. D. Mboyi, C. Maaliki, A. M. Makaya, Y. Canac, C. Duhayon, R. Chauvin, *Inorg. Chem.* **2016**, *55*, 11018-11027.
- [8] a) R. K. Oram, S. Trippett, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1300-1310; b) E. Evangelidou-Tsolis, F. Ramirez, *Phosphorus* **1974**, *4*, 121-127; c) D. Dakternieks, G. V. Roeschenthaler, R. Schmutzler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 507-510; d) D. Dakternieks, G. V. Roeschenthaler, R. Schmutzler, *Inst. Mond. Phosphate*, **1978**, pp. 591-597; e) G. V. Roeschenthaler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 131-135; f) Q.-C. Mir, R. W. Shreeve, J. n. M. Shreeve, *Phosphorus Sulfur Silicon Relat. Elem.* **1980**, *8*, 331-334.
- [9] P. W. N. M. Van Leeuwen, C. F. Roobeek, *Tetrahedron* **1981**, *37*, 1973-1983.
- [10] P. W. N. M. Van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1983**, *258*, 343-350.
- [11] a) R. S. Jolly, G. Luedtke, D. Sheehan, T. Livinghouse, *J. Am. Chem. Soc.* **1990**, *112*, 4965-4966; b) P. A. Wender, T. E. Jenkins, S. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 1843-1844; c) P. A. Wender, T. E. Smith, *J. Org. Chem.* **1996**, *61*, 824-825; d) M. Murakami, M. Ubukata, K. Itami, Y. Ito, *Angew. Chem., Int. Ed.* **1998**, *37*, 2248-2250; e) D. J. R. O'Mahony, D. B. Belanger, T. Livinghouse, *Org. Biomol. Chem.* **2003**, *1*, 2038-2040; f) K. Shen, T. Livinghouse, *Synlett* **2010**, 247-249; g) S. Huang, X. Li, C. L. Lin, I. A. Guzei, W. Tang, *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 2204-2206.
- [12] a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748-11749; b) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *Tetrahedron* **2008**, *64*, 6073-6081; c) S. Yanagisawa, K. Ueda, H. Sekizawa, K. Itami, *J. Am. Chem. Soc.* **2009**, *131*, 14622-14623; d) K. Ueda, S. Yanagisawa, J. Yamaguchi, K. Itami, *Angew. Chem., Int. Ed.* **2010**, *49*, 8946-8949, S8946/8941-S8946/8968; e) C. Meyer, D. Schepmann, S. Yanagisawa, J. Yamaguchi, K. Itami, B. Wuensch, *Eur. J. Org. Chem.* **2012**, *2012*, 5972-5979; f) R. Liu, G. N. Winston-McPherson, Z.-Y. Yang, X. Zhou, W. Song, I. A. Guzei, X. Xu, W. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 8201-8204; g) K. Ueda, K. Amaike, R. M. Maceiczky, K. Itami, J. Yamaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 13226-13232.
- [13] A. Tahara, Y. Miyamoto, R. Aoto, K. Shigetani, Y. Une, Y. Sunada, Y. Motoyama, H. Nagashima, *Organometallics* **2015**, *34*, 4895-4907.
- [14] Q. C. Mir, R. W. Shreeve, J. M. Shreeve, *Phosphorus Sulfur and Silicon and the Related Elements* **1980**, *8*, 331-333.
- [15] J. Senker, J. Ludecke, *Z. Naturforsch. B* **2001**, *56*, 1089-1099.
- [16] A. D. DeBellis, S. D. Pastor, G. Rihs, R. K. Rodebaugh, A. R. Smith, *Inorg. Chem.* **2001**, *40*, 2156-2160.
- [17] a) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841-861; b) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322-4326.
- [18] a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748-11749; b) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *Tetrahedron* **2008**, *64*, 6073-6081.
- [19] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286-2293.
- [20] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
- [21] K. Wu, A. G. Doyle, *Nature Chem.* **2017**, *9*, 779-784.
- [22] a) R. J. Thatcher, D. G. Johnson, J. M. Slattery, R. E. Douthwaite, *Chem. Eur. J.* **2012**, *18*, 4329-4336; b) J. Slattery, R. J. Thatcher, Q. Shi, R. E. Douthwaite, *Pure Appl. Chem.* **2010**, *82*, 1663-1671; c) Q. Shi, R. J. Thatcher, J. Slattery, P. S. Saari, A. C. Whitwood, P. C. McGowan, R. E. Douthwaite, *Chem. Eur. J.* **2009**, *15*, 11346-11360.
- [23] a) D. A. Valyaev, R. Brousses, N. Lugan, I. Fernández, M. A. Sierra, *Chem. Eur. J.* **2011**, *17*, 6602-6605; b) M. Fusè, I. Rimoldi, E. Cesarotti, S. Rampino, V. Barone, *Phys. Chem. Chem. Phys.* **2017**, *19*, 9028-9038.
- [24] a) G. Frenking, K. Wichmann, N. Fröhlich, J. Grobe, W. Golla, D. L. Van, B. Krebs, M. Läge, *Organometallics* **2002**, *21*, 2921-2930; b) S. H. Strauss, K. D. Abney, *Inorg. Chem.* **1984**, *23*, 515-516.
- [25] J. Apel, R. Bacher, J. Grobe, D. Le Van, *Z. Anorg. Allg. Chem.* **1979**, *453*, 39-52.
- [26] a) G. T. Andrews, I. J. Colquhoun, W. McFarlane, S. O. Grim, *J. Chem. Soc., Dalton Trans.* **1982**, 2353-2358; b) M. S. A. A. El-Mottaleb, *J. Mol. Struct.* **1976**, *32*, 203-205.
- [27] G. R. Dobson, P. M. Hodges, M. A. Healy, M. Poliakoff, J. J. Turner, S. Firth, K. J. Asali, *J. Am. Chem. Soc.* **1987**, *109*, 4218-4224.
- [28] F. H. Allen, *Acta Crystallogr. B* **2002**, *58*, 380.
- [29] C. Zhu, E. Gras, C. Duhayon, F. Lacassin, X. Cui, R. Chauvin, *Chemistry – An Asian Journal* **2017**, *12*, 2845-2856.
- [30] a) M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 11917-11924; b) M. Tokunaga, Y. Wakatsuki, *Angew. Chem. Int. Ed.* **1998**, *37*, 2867-2869; c) L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *Dalton Trans.* **2016**, *45*, 1717-1726; d) L. M. Milner, N. E. Pridmore, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *J. Am. Chem. Soc.* **2015**, *137*, 10753-10759; e) J. M. Lynam, L. M. Milner, N. S. Mistry, J. M. Slattery, S. R. Warrington, A. C. Whitwood, *Dalton Trans.* **2014**, *43*, 4565-4572; f) B. Breit, U. Gellrich, T. Li, J. M. Lynam, L. M. Milner, N. E. Pridmore, J. M. Slattery, A. C. Whitwood, *Dalton Trans.* **2014**, *43*, 11277-11285; g) D. G. Johnson, J. M. Lynam, N. S. Mistry, J. M. Slattery, R. J. Thatcher, A. C. Whitwood, *J. Am. Chem. Soc.* **2013**, *135*, 2222-2234; h) T. Naota, H. Takaya, S. I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599-2660.
- [31] K. Onitsuka, N. Dodo, Y. Matsushima, S. Takahashi, *Chem. Commun.* **2001**, 521-522.
- [32] J. A. Samuels, K. Folting, J. C. Huffman, K. G. Caulton, *Chem. Mater.* **1995**, *7*, 929-935.
- [33] a) R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) M. v. Arnim, A. R., *J. Chem. Phys.* **1999**, *111*, 9183-9190; c) P. Császár, P. Pulay, *J. Mol. Str.* **1984**, *114*, 31-34; d) P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535; e) P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511; f) K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; g) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theo. Chem. Acc.* **1997**, *97*, 119; h) T. Koga, H. Kobayashi, *J. Chem. Phys.* **1985**, *82*, 1437-1439; i) P. Pulay, *Chem. Phys. Lett.* **1980**, *23*, 393-398; j) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; k) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.



## Entry for the Table of Contents

## FULL PAPER

A comprehensive overview of the synthesis, stereoelectronic properties and coordination chemistry of large, electron-poor P(III) ligands bearing highly fluorinated alkoxides is described.



Sharifa Hussein, Denis Priester, Paul Beet, Jonathon Cottom, Sam J. Hart, Tim James, Robert J. Thatcher, Adrian C. Whitwood and John M. Slattery\*

Page No. – Page No.

Filling a niche in “ligand space” with bulky, electron-poor phosphorus (III) alkoxides